mations were done by measuring the optical density of their methanolic solutions; yields are given in Table VI.

Product Distribution as a Function of the Aniline Concentration. The experiment was performed with aniline and *p*-nitroaniline, the concentration range being between 0.1 and 13% w/w. The yields of nitrobenzene and *p*-dinitrobenzene were 12.5 ± 0.5 and 5.5 ± 0.5%, respectively, in all concentrations. At concentrations above 0.5, increasing amounts of dark viscous polymers and formic acid were eluted with a mixture of methanol–ethyl acetate (1:1). Water extract of the silica gel gave positive test for nitrate ions (precipitation in the presence of nitron solution[13]).

Ozonation of Formic Acid. Silica gel, adsorbed with pure formic acid (1%), was saturated with ozone at −78 °C. The outlet gas was allowed to bubble through a aqueous barium hydroxide solution. A white precipitate of barium carbonate indicated the formation of carbon dioxide. After 0.5 h 47% of formic acid was regenerated by ether extraction of the silica gel.

Registry No.—Anisole, 100-66-3; 1-nitropropane, 108-03-2.

References and Notes

(1) (a) P. S. Bailey and J. E. Keller, *J. Org. Chem.*, **33**, 2680 (1968); (b) P. S. Bailey, T. P. Carter, and L. M. Southwick, *ibid.*, **37**, 2997 (1972).
(2) (a) P. S. Bailey, J. E. Keller, D. A. Mitchard, and H. M. White, *Adv. Chem. Ser.*, **77**, 58 (1968); (b) P. S. Bailey, D. A. Mitchard, and A. Y. Kashab, *J. Org. Chem.*, **33**, 2675 (1968); (c) P. S. Bailey, J. E. Keller, and T. P. Carter, *ibid.*, **35**, 2777 (1970); (d) P. S. Bailey and J. E. Keller, *ibid.*, **35**, 2782 (1970).
(3) G. B. Bachman and K. G. Strawn, *J. Org. Chem.*, **33**, 313 (1968).
(4) Z. Cohen, E. Keinan, Y. Mazur, and T. H. Varkony, *J. Org. Chem.*, **40**, 2141 (1975).
(5) M. J. Rozen and C. Eden, *J. Phys. Chem.*, **74**, 2303 (1970).
(6) H. M. White and P. S. Bailey, *J. Org. Chem.*, **30**, 3037 (1965).
(7) J. E. Batterbee and P. S. Bailey, *J. Org. Chem.*, **32**, 3899 (1967).
(8) D. Lerdal, Ph.D. Dissertation, The University of Texas at Austin, 1971.
(9) C. C. Price and A. L. Tumolo, *J. Am. Chem. Soc.*, **86**, 4691 (1964).
(10) F. E. Stary, D. E. Emge, and R. W. Murray, *J. Am. Chem. Soc.*, **98**, 1880 (1976).
(11) W. D. Emmons, *J. Am. Chem. Soc.*, **76**, 3470 (1954).
(12) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5528 (1957).
(13) P. Kolsaker and B. Teige, *Adv. Chem. Ser.*, **112**, 101 (1972).
(14) A. I. Vogel, "Quantitative Inorganic Analysis", 3d ed. Longmans, Green and Co., New York, N.Y., 1961, p 583.

Study on the Adduct of Ketenimine and Aziridine

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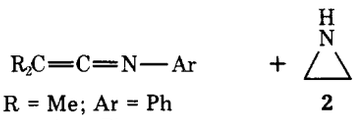
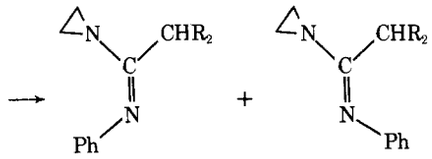
The reaction of *N*-arylketenimines **1a–c** with aziridine gave the imidoylaziridines **3a–c** in excellent yields. However. *N*-cyclohexylketenimine **1d** gave the rearranged product, the imidazoline **5d.** Syn–anti isomerism of the imidoylaziridines was found by NMR spectroscopy. Acidic treatment of **3a,b** in ethanol resulted in ring expansion to the imidazolines **5a,b** or addition of the solvent to the aziridine ring according to acids. Diphenylketene cycloadded to the C=N bond of the imidoylaziridine **3a,** while no reaction with phenyl isocyanate and phenyl isothiocyanate was observed.

For preparative purposes the addition of aziridine to heterocumulenes followed by ring expansion seems to provide a convenient method.[1] This reaction seems not to have been studied. In the present paper we report the addition of ketenimines with aziridine and some chemical properties of the adducts, imidoylaziridines.[2] We also discuss syn–anti isomerism of the imidoylaziridines by NMR spectroscopy.

Preparation and Syn–Anti Isomerism. The reactions of *N*-arylketenimines **1a–c** with aziridine (**2**) gave imidoylaziridines **3a–c** quantitatively at room temperature. On the other hand, preparation of **3a** from *N*-phenylisobutyrimidoyl chloride and aziridine was not successful because of ring expansion of the expected aziridine during workup. Therefore



1a, R = Me; Ar = Ph
b, R = Ar = Ph
c, R = Ph; Ar = *p*-$CH_3C_6H_4$

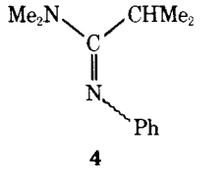


	syn	anti[a]
3a	52%	48%
3b	68	32
3c	73	27

[a] Determined by NMR at 23 °C in $CDCl_3$.

the reaction of ketenimines is superior to the other method with respect to avoiding contaminants and handling with unstable aziridines. The isolated products consisted of syn and anti isomers.

The NMR spectrum of **3a** (at 23 °C) had two singlets at δ 1.82 and 2.15, which were assigned to the protons of the aziridine ring. The methyl protons exhibited two doublets at δ 1.15 and 1.27. At 100 °C, the signals of aziridinyl and methyl protons converted into one singlet at δ 1.94 and one doublet at δ 1.18 (in Me_2SO-d_6), respectively. These signals returned to the original pattern by lowering the temperature. Though aziridinyl protons are often observed as multiplets, rapid inversion of the aziridine ring caused the four ring protons to become equivalent in this case. The signal of aziridinyl protons of the syn isomer appeared in lower field than that of the anti isomer because of the shielding effect of the phenyl group lying close to the aziridine ring. In comparison with the adduct **4**

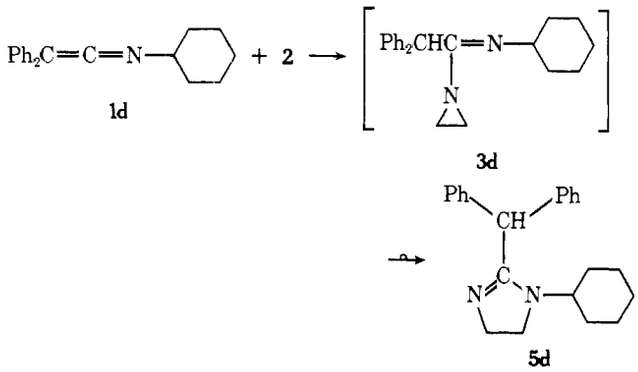


4

from dimethylamine and the ketenimine **1a,** whose NMR spectrum showed only one set of isopropyl and *N*-methyl signals at 23 °C,[3] syn–anti isomerization of **3a** was slower than that of **4.** The rate of the isomerization seemed to depend on the electron-donating ability of the amino group to the C=N bond.

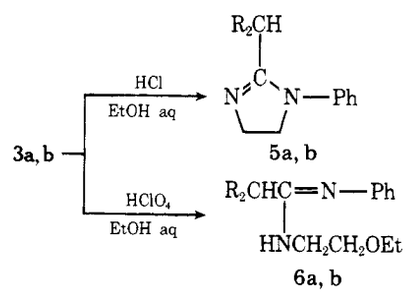
Similar phenomena were observed in the NMR spectra of the adducts **3b** and **3c**, and the ratios of syn and anti isomers were 68:32 and 73:27, respectively. The syn–anti ratio was dependent on the extent of steric repulsion between Ar and R of **3**.

In the case of the ketenimine **1d**, the addition of aziridine did not occur at room temperature, whereas the addition was accomplished by heating at 80 °C for 150 h in benzene. The difference in reactivity between *N*-arylketenimine and *N*-cyclohexylketenimine was considered to be due to the electron deficiency of the central carbon atom of the cumulative system.[4] The product obtained was the imidazoline **5d**, which showed the C=N absorption at 1630 cm^{-1} in the IR spectrum and two multiplets, assigned to the ring methylene protons, at δ 3.1–3.4 and 3.6–3.8 in the NMR spectrum. Low-field shift of the methylene protons indicated the ring cleavage of the aziridine ring and rearrangement to the imidazoline **5d** as described below.



Alcoholysis and Rearrangement of the Adducts. A three-membered ring attached to a double bond often rearranges to a five-membered ring compound upon heating or by treating with catalysts.[1,5]

The acidic treatments of the adducts **3** in aqueous ethanol yielded the different products according to the nature of the acids. With hydrochloric acid, the aziridines **3a** and **3b** rearranged to the imidazolines **5a** and **5b** quantitatively. In the IR spectra, the C=N absorptions appeared between 1610 and 1605 cm^{-1}. The NMR spectra of **5a** and **5b** showed multiplets at δ 3.7–3.8 and 3.7–4.0, respectively. This type of rearrangement was previously reported by Heine.[2]



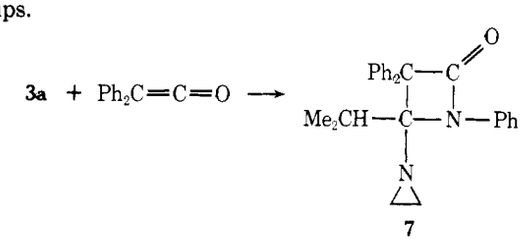
a, R = Me
b, R = Ph

Though hydrochloric acid caused the ring expansion of the aziridine ring, perchloric acid led to addition of the alcohol to the aziridine ring of **3** without the formation of **5**. The products **6a** and **6b** showed the C=N absorptions at 1620 and 1615 cm^{-1}, respectively. The NMR spectra of the products fully supported the structures.

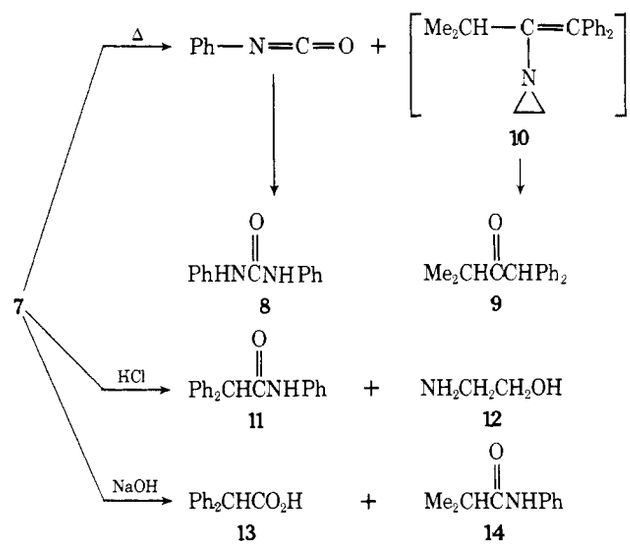
The thermal rearrangement of **3d** to **5d** was observed in the course of the reaction. On the other hand, the treatment of **3a** in refluxing toluene did not cause the rearrangement. This may be due to difference in nucleophilicity of the nitrogens of the imino functions.

Cycloadduct with Diphenylketene. The cycloaddition of heterocumulenes to azomethines[6] or 1-substituted aziridines[7] has been investigated. With azomethines, 1,2-cycloaddition occurred across the C=N bond, and 1,3-cycloaddition reaction involving ring cleavage was observed for 1-substituted aziridines. The compound **3** has both a C=N and an aziridinyl group; therefore, it is interesting to know which function of **3** will initiate the reaction with heterocumulenes.

Phenyl isocyanate and phenyl isothiocyanate did not react with the aziridine **3a** even in refluxing benzene. However, diphenylketene reacted with **3a** at room temperature to give the 1:1 adduct, the azetidine **7**, formed by the addition of the ketene across the C=N bond of **3a**. No cycloadduct was obtained in the reaction of the aziridine **3b** and the ketene. This was presumably because of the steric effect of the phenyl groups.



The structure of **7** was supported by pyrolysis and hydrolyses. Pyrolysis of **7** gave phenyl isocyanate, which was identified as *N,N'*-diphenylurea (**8**, 72%), and diphenylmethyl isopropyl ketone (**9**, 80%). The compound **9** was formed by hydrolysis of the enamine **10** during column chromatography.



Acidic hydrolysis of the compound **7** afforded diphenylacetanilide (**11**, 98%) and 2-aminoethanol (**12**). Alkaline hydrolysis of the azetidine **7** gave diphenylacetic acid (**13**, 68%) and isobutyranilide (**14**, 85%).

Experimental Section

All melting points were determined on a Yanagimoto micromelting point apparatus and were uncorrected. IR, NMR, and mass spectra were obtained on a JASCO IR-E spectrometer, JEOL LNM-3H-60 and JNM-PS-100 spectrometers, and a Hitachi RMU-6E spectrometer, respectively.

As contact with aziridine should be avoided, all the procedures were carried out in a draft chamber.

Materials. Ketenimines **1a**,[8] **1b**, and **1c**[9] were prepared by the reported methods. Commercially available aziridine was distilled over sodium hydroxide prior to use.

Reaction of Dimethylketene-*N*-phenylimine (1a) and Aziridine (2). To a solution of the ketenimine **1a** (2.7 g, 19 mmol) in ether (25 ml), 1.5 g (35 mmol) of **2** was added dropwise with cooling. The

reaction occurred exothermically and soon the characteristic infrared absorption of the ketenimine disappeared. After 15 min, the solvent and excess aziridine were evaporated in vacuo. Distillation of the residue gave 3.4 g (97%) of *N*-phenylisobutyrimidoylaziridine (**3a**): bp 82–85 °C (2 mm); IR (neat) 1625 cm^{-1} (C=N); NMR ($CDCl_3$, 23 °C) δ 1.15 (d, 3.1, J = 7.5 Hz, syn Me), 1.27 (d, 2.9, J = 7.5 Hz, anti Me), 1.82 (s, 1.9, anti aziridinyl protons), 2.15 (s, 2.1, syn aziridinyl protons), 2.4–2.8 (m, 1, J = 7.5 Hz, C**H**Me_2), 6.5–7.4 (m, 5, aromatic protons), the ratio of syn and anti isomers was 52:48 [(Me_2SO-d_6, 100 °C) 1.18 (d, 6, J = 7.5 Hz, 2 Me), 1.94 (s, 4, aziridinyl protons), 2.72 (septet, 1, J = 7.5 Hz, C**H**Me_2), 6.4–7.4 (m, 5, aromatic protons)]; mass spectrum m/e 188 (M^+, calcd 188).

Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found; C, 76.66; H, 8.84; N, 14.94.

Reaction of Diphenylketene-*N*-phenylimine (1b) and Aziridine (2). The ketenimine **1b** (2.7 g, 10 mmol) was treated with **2** (0.64 g, 15 mmol) in ether (25 ml) at 25 °C and the characteristic IR absorption of **1b** disappeared immediately. Pale yellow crystalline 1-(*N*-phenyldiphenylacetimidoyl)aziridine (**3b**, 3.1 g, 99%) was obtained upon evaporation of the solvent. Recrystallization of **3b** from ethanol gave colorless needles: mp 103–105 °C; IR (Nujol) 1630 cm^{-1} (C=N); NMR ($CDCl_3$, 23 °C) δ 1.80 (s, 2.7, syn aziridinyl protons), 1.82 (s, 1.3, anti aziridinyl protons), 5.14 (s, 0.7, syn C**H**Ph_2), 5.19 (s, 0.3, anti C**H**Ph_2), 6.5–7.5 (m, 15, aromatic protons), the ratio of syn and anti isomers was 68:32 [(Me_2SO-d_6, 100 °C) 1.81 (s, 4, aziridinyl protons), 5.12 (s, 1, C**H**Ph_2), 6.7–7.5 (m, 15 aromatic protons)]; mass spectrum m/e 312 (M^+, calcd 312).

Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.66; H, 6.60; N, 8.96.

Reaction of Diphenylketene-*N*-*p*-tolylimine (1c) and Aziridine (2). After the same treatment as described above, the reaction of 5.7 g (20 mmol) of **1c** and 1.3 g (30 mmol) of **2** gave 5.4 g (83%) of 1-(*N*-*p*-tolyldiphenylacetimidoyl)aziridine (**3c**), which was recrystallized from ethanol to give colorless needles: mp 138–139 °C; IR (Nujol) 1620 cm^{-1} (C=N); NMR ($CDCl_3$, 23 °C) δ 1.80 (s, 2.9, syn aziridinyl protons), 1.81 (s, 1.1, anti aziridinyl protons), 2.25 (s, 3, Me), 5.15 (s, 0.7, syn C**H**Ph_2), 5.23 (s, 0.3, anti C**H**Ph_2), 6.4–7.4 (m, 14, aromatic protons), the ratio of syn and anti isomers was 73:27; mass spectrum m/e 326 (M^+, calcd 326).

Anal. Calcd for $C_{23}H_{22}N_2$: C, 84.62; H, 6.79; N, 8.58. Found: C, 84.52; H, 6.77; N, 8.30.

Reaction of Diphenylketene-*N*-cyclohexylimine (1d) and Aziridine (2). A mixture of the ketenimine **1d** (2.8 g, 10 mmol) and **2** (0.85 g, 20 mmol) in benzene (20 ml) was stirred for 8 h at room temperature. As no change was observed in the IR spectrum, the mixture was heated to reflux for 150 h until the characteristic absorption of **1d** disappeared. After removal of the solvent and excess aziridine, 3.0 g (94%) of 2-diphenylmethyl-3-cyclohexylimidazoline (**5d**) was isolated by adding petroleum ether, and was recrystallized from hexane to give colorless needles: mp 75–76 °C; IR (Nujol) 1630 cm^{-1} (C=N); NMR ($CDCl_3$) δ 0.8–1.8 [m, 10, $(CH_2)_5$], 3.1–3.4 (m, 3, CH and CH_2), 3.6–3.8 (m, 2, CH_2), 4.87 (s, 1, C**H**Ph_2), 7.1–7.3 (m, 10, aromatic protons); mass spectrum m/e 318 (M^+, calcd 318).

Anal. Calcd for $C_{22}H_{26}N_2$: C, 82.97; H, 8.23; N, 8.80. Found: C, 82.98; H, 8.29; N, 8.77.

Preparation of the Amidine 4. An excess amount of gaseous dimethylamine was bubbled into an ethereal solution of dimethylketene-*N*-phenylimine (2.1 g) at room temperature. After the characteristic IR absorption of the ketenimine had disappeared, the solvent was removed and the residue was distilled to give 2.6 g (95%) of N^1,N^1-dimethyl-N^2-phenylisobutyramidine (**4**): bp 75–78 °C (1 mm); IR (neat) 1615 (shoulder), 1595, and 1585 cm^{-1}; NMR ($CDCl_3$, 23 °C) δ 1.10 (d, 6, J = 7.5 Hz, CH**M**e_2), 2.92 (s, 6, NMe_2), 3.10 (septet, 1, J = 7.5 Hz, C**H**Me_2), 6.5–7.2 (m, 5, aromatic protons); mass spectrum m/e 190 (M^+, calcd 190).

Anal. Calcd for $C_{12}H_{18}N_2$: C, 75.74; H, 9.54; N, 14.72. Found: C, 75.89; H, 9.51; N, 14.78.

Rearrangement of the Aziridine 3a with Hydrochloric Acid. A mixture of 6 N hydrochloric acid (4 ml), ethanol (20 ml), and 1.8 g of **3a** was kept refluxing for 5 h. The mixture was neutralized with aqueous NaOH solution and extracted with ether. The organic layer was dried (Na_2SO_4), concentrated, and distilled to give 1.36 g (76%) of 2-isopropyl-3-phenylimidazoline (**5a**): bp 77 °C (1 mm); IR (neat) 1610 cm^{-1} (C=N); NMR ($CDCl_3$) δ 1.10 (d, 6, J = 7.0 Hz, 2 Me), 2.61 (septet, 1, J = 7.0 Hz, C**H**Me_2), 3.7–3.8 [m, 4, $(CH_2)_2$], 7.0–7.4 (m, 5, aromatic protons); mass spectrum m/e 188 (M^+, calcd 188).

Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.47; H, 8.70; N, 14.85.

Rearrangement of the Aziridine 3b with Hydrochloric Acid. The aziridine **3b** (0.6 g) was treated under the same conditions as above to give 0.26 g (43%) of 2-diphenylmethyl-3-phenylimidazoline (**5b**). Recrystallization from ethanol gave colorless granules: mp 111–113 °C; IR (Nujol) 1605 cm^{-1} (C=N); NMR ($CDCl_3$) δ 3.7–4.0 [m, 4, $(CH_2)_2$], 5.95 (s, 1, C**H**Ph_2), 6.8–7.3 (m, 15, aromatic protons); mass spectrum m/e 312 (M^+, calcd 312).

Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.52; H, 6.57; N, 9.03.

Alcoholysis of the Aziridine 3a with Perchloric Acid. A mixture of 1.0 g of the aziridine **3a**, 1.5 ml of 40% perchloric acid, and 20 ml of ethanol was heated to reflux for 5 h. The mixture was neutralized (NaOH aqueous), extracted (ether), and concentrated to give 0.95 g (79%) of N^1-2-ethoxyethyl-N^2-phenylisobutyramidine (**6a**), which was purified by pot distillation (75 °C, 1 mm): IR (neat) 3400–3300 (NH), 1620 cm^{-1} (C=N); NMR ($CDCl_3$) δ 1.05 (d, 6, J = 7.0 Hz, CH**M**e_2), 1.21 (t, 3, J = 7.5 Hz, CH_2**M**e), 2.74 (septet, 1, J = 7.0 Hz, C**H**Me_2), 3.3–3.7 [m, 6, $(CH_2)_2$ and CH_2], 4.5–4.8 (broad, 1, NH), 6.6–7.3 (m, 5, aromatic protons); mass spectrum m/e 234 (M^+, calcd 234), 161 ($M^+ - CH_2CH_2OEt$).

Anal. Calcd for $C_{14}H_{22}N_2O$: C, 71.75; H, 9.46; N, 11.96. Found: C, 72.03; H, 9.45; N, 12.51.

Alcoholysis of the Aziridine 3b with Perchloric Acid. From 0.60 g of the aziridine **3b**, 0.49 g (82%) of crude N^1-2-ethoxyethyl-N^2-phenyldiphenylacetamidine (**6b**) was obtained by the same treatment as above. The compound **6b** was recrystallized from hexane to afford colorless needles: mp 129–130 °C; IR (Nujol) 3320 (NH) and 1615 cm^{-1} (C=N); NMR ($CDCl_3$) δ 1.08 (t, 3, J = 7.0 Hz, Me), 3.39 (q, 2, J = 7.0 Hz, CH_2), 3.4–3.6 [m, 4, $(CH_2)_2$], 4.5–4.8 (broad, 1, NH), 6.5–7.3 (m, 15, aromatic protons); mass spectrum m/e 358 (M^+, calcd 358), 285 ($M^+ - CH_2CH_2OEt$).

Anal. Calcd for $C_{24}H_{26}N_2O$: C, 80.41; H, 7.31; N, 7.82. Found: C, 80.22; H, 7.53; N, 7.78.

Reaction of the Aziridine 3a and Diphenylketene. To a solution of 5.0 g (27 mmol) of the aziridine **3a** in benzene, 5.2 g (27 mmol) of diphenylketene was added dropwise. The mixture was stirred at room temperature for 15 min until the characteristic IR absorption of the ketene disappeared. The mixture was concentrated in vacuo to give 6.5 g (64%) of 1,3,3-triphenyl-4-isopropyl-4-(1-aziridinyl)azetidin-2-one (**7**), which was recrystallized from benzene–hexane: colorless granules; mp 147–148 °C; IR (Nujol) 1740 cm^{-1} (C=O); NMR ($CDCl_3$) δ 0.82 (d, 3, J = 6.5 Hz, Me), 1.16 (d, 3, J = 6.5 Hz, Me), 1.2–1.4 and 1.6–1.8 (m, 2, aziridinyl protons, respectively), 2.5–2.9 (m, 1, J = 6.5 Hz, C**H**Me_2), 7.2–7.6 and 7.8–8.0 (m, 15, aromatic protons); mass spectrum m/e 382 (M^+, calcd 382), 263 ($M^+ - PhNCO$), 188 ($M^+ - Ph_2CCO$).

Anal. Calcd for $C_{26}H_{26}N_2O$: C, 81.64; H, 6.85; N, 7.32. Found: C, 81.92; H, 6.80; N, 7.30.

Pyrolysis of the Azetidine 7. The azetidine **7** (2.0 g, 5 mmol) was heated for 2 h in refluxing toluene (25 ml). The resulting phenyl isocyanate was distilled off under reduced pressure and led to *N*,*N*′-diphenylurea (**8**) by addition of aniline. The urea **8** was recrystallized from ethanol to give colorless needles (72%). The IR spectrum of **8** was in fair agreement with that of an authentic sample and no depression of melting point was observed for the mixture of **8** and the authentic sample. The residue was chromatographed (Al_2O_3, benzene–hexane) to isolate 1.0 g (80%) of diphenylmethyl isopropyl ketone (**9**), which was recrystallized (ethanol) to give colorless needles: mp 78–79 °C; IR (Nujol) 1690 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.07 (d, 6, J = 7.5 Hz, 2 Me), 2.77 (septet, 1, J = 7.5 Hz, (C**H**Me_2), 5.25 (s, 1, C**H**Ph_2), 7.1–7.3 (m, 10, aromatic protons); mass spectrum m/e 238 (M^+, calcd 238).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.47; H, 7.58.

Acidic Hydrolysis of the Azetidine 7. An alcoholic solution of 2.0 g (5 mmol) of the azetidine **7** and 4 ml of 6 N hydrochloric acid was kept refluxing for 5 h. The mixture was poured into water and extracted with ether. From the organic layer, 1.5 g (98%) of diphenylacetanilide (**11**) was obtained. Recrystallization of **11** from ethanol afforded colorless needles, mp 191–192 °C. The IR spectrum of **11** agreed with that of an authentic sample prepared from diphenylacetyl chlolide and aniline, and the melting point of **11** was not depressed by mixing with the authentic sample. The aqueous layer was made alkaline (sodium hydroxide) and extracted (ether). The extract contained 2-aminoethanol (**12**), which was identified by GLC.

Alkaline Hydrolysis of the Azetidine 7. An alcoholic solution of the azetidine **7** (2.0 g) and 2 N sodium hydroxide (12 ml) was refluxed for 6 h. The mixture was extracted (ether) after addition of water. From the ethereal layer, 0.72 g (85%) of isobutyranilide (**14**) was isolated, and was recrystallized from ethanol to give colorless needles, mp 110–111 °C. The IR spectrum of **14** agreed with that of an authentic sample prepared from corresponding acid chloride and aniline, and the melting point of **14** was not depressed by mixing with the

authentic sample. The aqueous layer was acidified (hydrochloric acid) and extracted (ether). Evaporation of ether gave 0.41 g (68%) of diphenylacetic acid (13). Recrystallization of 13 from benzene gave colorless granules, mp 147–148 °C. The melting point and IR spectrum of 13 were in good agreement with those of an authentic sample.

Registry No.—1a, 14016-34-3; 1b, 14181-84-1; 1c, 5110-45-2; 1d, 24932-57-8; 2, 151-56-4; *syn*-3a, 61047-06-1; *anti*-3a, 61047-07-2; *syn*-3b, 61047-08-3; *anti*-3b, 61047-09-4; *syn*-3c, 61047-10-7; *anti*-3c, 61047-11-8; 4, 29172-31-4; 5a, 61047-12-9; 5b, 61047-13-0; 5d, 61047-14-1; 6a, 61047-15-2; 6b, 61047-16-3; 7, 61047-17-4; 9, 7495-04-7; 11, 4695-14-1; 14, 4406-41-1; dimethylamine, 124-40-3; diphenylketene, 525-06-4.

References and Notes

(1) O. C. Dermer and G. E. Ham, "Ethylenimine and Other Aziridines", Academic Press, New York, N.Y., 1966, pp 193–194 and 280–293.
(2) H. W. Heine and H. S. Bender, *J. Org. Chem.*, **25**, 461 (1960).
(3) The NMR spectrum of N^1,N^1-dimethyl-N^2-phenyldiphenylacetamidine also showed only one singlet of the methyl protons, indicative of fast syn–anti isomerization.
(4) N. Murai, M. Komatsu, Y. Ohshiro, and T. Agawa, *J. Org. Chem.*, **42**, 448 (1977).
(5) Y. Bahurel, L. Cottier, and G. Descotes, *Synthesis*, 118 (1974).
(6) H. Ulrich, "Cycloaddition Reaction of Heterocumulenes", Academic Press, New York, N.Y., 1967, pp 76–83, 153–159, and 227–235.
(7) E. Gulbins, R. Morlock, and K. Hamman, *Justus Liebigs Ann. Chem.*, **698**, 180 (1966); A. P. Sineokov, F. N. Gladysheva, and V. S. Etlis, *Khim. Geterotsikl. Soedin.*, **611** (1970); *Chem. Abstr.*, **73**, 66351 (1970).
(8) C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **76**, 4398 (1954).
(9) C. L. Stevens and H. Singhal, *J. Org. Chem.*, **29**, 34 (1964).

Acid-Catalyzed Addition of Secondary Amines to Cyclopropyl Ketones. Mass Spectra of Some Cyclic Aminobutyrophenones

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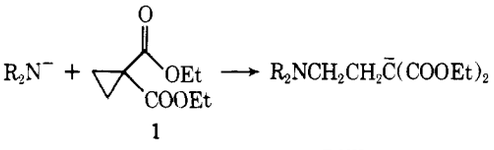
Four cyclic secondary amines [morpholine (**a**), piperidine (**b**), pyrrolidine (**c**), and 2-(1-piperazinyl)ethanol (**d**)] were induced to react with five cyclopropyl ketones of the structure RCO-c-C_3H_5 (**16–20**, R = *p*-anisyl, phenyl, *p*-chlorophenyl, methyl, and cyclopropyl, respectively) in presence of acid to yield ring-opened γ-amino ketones (**21–27**). The products were characterized by their spectroscopic properties (IR, UV, NMR, and MS), derivatives, and other analytical data. The reactivity of the ketones increases in the order cyclopropyl < *p*-anisyl < phenyl < *p*-chlorophenyl. Since this cannot be reconciled with a cyclopropylcarbinyl–homoallylic cation mechanism, the intermediacy of a carbinolamine (**31**) is invoked.

Our studies concerning addition of organomagnesium halides to cyclopropyl ketones,[1] which were accompanied by ring opening, directed our interest to examining the behavior of these ketones toward other nucleophiles such as secondary amines.

Stewart and co-workers[2] have shown that secondary amines add to 1,1-disubstituted cyclopropanes **1** bearing two electron-withdrawing groups in a 1,4 fashion, leading to ring-opened γ-amino esters **2**. The highly conjugated ("bisected")



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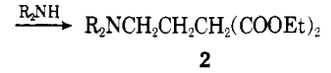


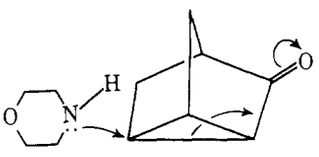
2

nortricyclanone **3** was shown[3] to add morpholine in a 1,4 manner to give exclusively *exo*-5-*N*-morpholinobicyclo[2.2.1]heptan-2-one (**4**), indicating ring rupture by backside nucleophilic attack.

Acid-induced addition of secondary amines to cyclopropanes substituted by carbonyl groups was demonstrated by Cook et al.,[4] who obtained diamino- and aminoimonium salt products (**5** and **6**) from nortricyclanone and pyrrolidine or hexamethylenimine in presence of acids.

The sequence of incorporation of the amines is not known; the role of the catalyst is, apparently, in a dehydration stage.

Direct attack on the carbonyl carbon without ring opening was demonstrated by Cook et al.,[4] on treating nortricyclanone



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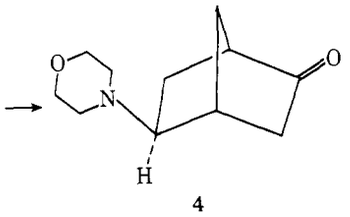

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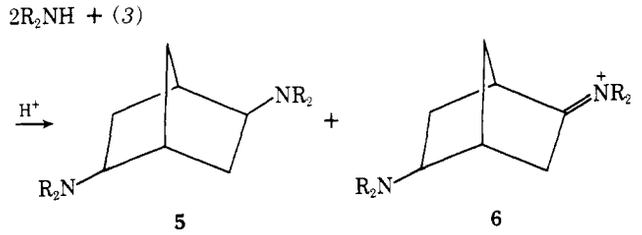

5 6

with amine salts rather than with free nucleophilic amines, followed by $LiAlH_4$ reduction (**3** → **7**). They have also obtained[5] ring-retained products from cyclopropanecarboxaldehyde and methyl cyclopropyl ketone in presence of basic and acidic catalysts, respectively.

A rather esoteric reaction of ammonia with 1,1-dicarbethoxy-2,2,3,3-tetracyanocyclopropane (**8**) was reported by Regan.[6] Although the ring becomes highly deficient of elec-